COATINGS. ENAMELS

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DEVELOPMENT OF MULTICOMPONENT SUSPENSIONS FOR CATALYTIC COATINGS FOR BLOCK CERAMIC SUPPORTS

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The compositions of multicomponent boehmite suspensions in the pH range of the dispersion medium from 1.5 to 5.4 and methods of stabilizing cerium- and platinum-containing suspensions and application on a block cordierite support were investigated. The optimum conditions of preparing the suspensions and single-stage production of highly porous, strong, and uniform coatings of the Pt – CeO_2 – γ-Al_2O_3 system with a high yield and specific surface area of 150 – 170 m^2/g were established.

The problem of obtaining effective nanostructural oxide catalytic coatings containing nanoparticles of platinum-group metals on block supports of cordierite and other thermostable ceramic materials used in systems for treating exhaust gases from internal combustion engines is still pressing both in our country and abroad due to the increasing environmental protection requirements [1]. The existing methods of manufacturing such coatings are usually multistage, power- and labor-intensive, and the coatings frequently insufficiently adhere to the surface of the block ceramic support (BCS) and require high consumption of materials. The use of suspensions based on aluminum oxides and hydroxides with pH ~ 9.5 allows obtaining a high specific surface area of the coatings — up to 200 – 250 m^2/g, but impregnation of BCS must be repeated from 2 – 3 to 6 times with heat treatments after each application [2, 3].

We developed the methodological principles for single-stage production of multicomponent highly porous coatings on a matrix of mixed Ce and Al oxides containing nanoparticles of metallic platinum on block cordierite supports with the suspension method. Removing air from the suspension paste is one of the basic factors in eliminating defects in ceramic coatings [4], so that special attention was focused on studying the effect of degassing on the properties of the suspensions and coatings.

All coatings based on γ-Al_2O_3 – CeO_2 and Pt – γ-Al_2O_3 – CeO_2 systems were fabricated on the surfaces of the channels in a block cordierite, $(MgFe^{2+})_2Al_4Si_5O_{18}$, support with straight channels (66 per cm^3). The block channel section area was about 1 mm^2 and the wall thickness was about 150 µm. Boehmite — $AlO(OH) \cdot nH_2O$ — with a specific surface area of 300 to 380 m^2/g is the only solid phase in the suspension. Platinum was added to the suspension in the form of chloroplatinic acid (CPA), $H_2PtCl_6 \cdot H_2O$, cerium was incorporated in the form of the salt $Ce(NO_3)_3 \cdot 6H_2O$, and pH = 1.5 was maintained by addition of nitric acid. The use of $Ce(NO_3)_3 \cdot 6H_2O$ salt was due to the high mass content of cerium oxide in it (40%), high solubility in water, and low decomposition temperature (150 – 200°C), which facilitates preparation of the suspensions and heat treatment and also increases the yield of the coating.

The coatings were prepared by immersion and impregnation of the BCS with an aqueous suspension containing all of the required components of the catalytic coating and also a disaccharide (maltose) as a reducing and aggregating agent. After impregnation of the block, the residues of the suspension were removed by centrifugation and the block was then treated with heat at 550°C. The viscosity of boehmite suspensions with different dispersion media was investigated to determine the optimum composition of the suspensions. The suspensions were homogenized during mixing and degassing. Degassing was conducted in a 96 kPa vacuum at 20 – 25°C. The viscosity was determined indirectly with the flow time of 100 ml of the suspension from a cylindrical container through an opening 2 mm in diameter and 2 mm high.

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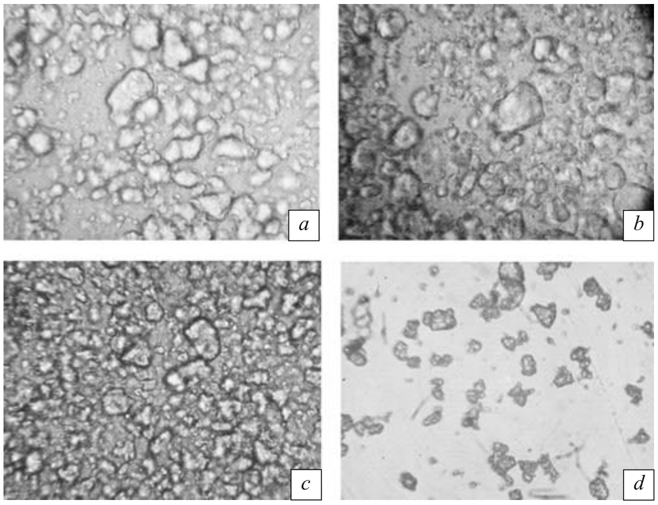

Fig. 1. Microstructure of particles of solid phase in aqueous suspensions of boehmite (length of largest grain: 32 – 36 μm) at pH = 5.4 without degassing (*a*), with degassing for 10 min (*b*) and 30 min (*c*) and initial boehmite (*d*).

The catalytic coatings of the Pt – CeO_2 – γ-Al_2O_3 system on BCS were prepared with a content of 1.5 g Pt per 1 dm^3 BCS and an $Al_2O_3 : CeO_2$ mass ratio in the coating from 1 : 0.1 to 1 : 2 at a constant content of maltose and CPA in the dispersion medium and incorporation of the calculated amount of cerium nitrate and boehmite in the suspension. The yield of coating was 6 – 7% of the final weight of the block with the coating. These samples were tested in laboratory conditions in a continuous unit in the reaction of oxidation of CO by oxygen in model gas mixtures of the composition (volume content, %): 0.3 CO, 0.3 – 1.0 O_2, remainder N_2 at a gas load of 10,000 – 20,000 m^3/h per 1 m^3 of catalyst with evaluation of the activity based on the degree of conversion of CO into CO_2 as a function of the temperature [2].

The phase composition was investigated for the coatings and catalysts by x-ray phase analysis on a SHIMADZU XRD-6000 and petrographically in a POLAM L-213 polarizing microscope in transmitted light; the specific surface area was determined with the Brunauer – Emmet – Teller method on a TriStar 3000 analyzer; the quantitative composition was determined by atomic emission spectrometry with inductively bound plasma on a Jobin Yvon spectrometer; the catalytic activity in the reaction of oxidation of CO by oxygen was investigated on a continuous laboratory unit using a OPTOGAZ-500.1 gas analyzer.

The initial compounds for fabricating the coatings were selected based on their high yield of oxides and low decomposition temperature. The initial substances added to the dispersion medium should have high solubility in water. The use of boehmite in the suspension instead of aluminum hydroxides and salts was due to its high specific surface area and yield of Al_2O_3 (85%), which increased the adhesion and yield of coating and decreased shrinkage of the coating in sintering. The use of $Ce(NO_3)_3 \cdot 6H_2O$ salt was due to the high yield of cerium oxide (40%), high solubility in water, and low decomposition temperature (150 – 200°C), which facilitated preparation of the suspensions and heat treatment. A disaccharide — maltose — was used as the reducing and aggregating agent due to its milder reducing properties and higher solubility in comparison to glucose [5].

Elimination of air from the suspension is a basic factor in eliminating defects in ceramic coatings [4], so that special attention was focused on studying the effect of degassing on the properties of the suspensions and coatings. In degassing the aqueous suspensions, we found that most of the air was removed in 10 – 15 min. This was manifested by turbulent release of air bubbles from the bulk of the suspension. However, increasing the degassing time to 30 min increased the homogeneity of the suspension (Fig. 1) which in turn positively affected the quality and yield of the coating. The experimental data on the effect of the degassing time for aqueous suspensions of boehmite on the mass yield of coatings on BCS are reported in Table 1. Degassing the suspension for 30 min increased the yield of coating on the BCS by 30%.

The studies of the optimum composition of the suspension were conducted with the data from measuring the flow time of 100 ml of the suspension from a cylindrical container through an opening 2 mm in diameter and 2 mm high. The results obtained are shown in Fig. 2. It was experimentally established that the maximum mass content of solid phase (boehmite) in the aqueous solution was 25% (point *d* in Fig. 2) for a flow time of 70 sec. When cerium nitrate and maltose were added to the dispersion medium, the viscosity of the suspensions increased sharply. The optimum composition of the multicomponent suspensions corresponded to the points of intersection of the flow curves and the straight line drawn parallel to the abscissa at the level of the established value of the maximum flow time, 70 sec. Point *b* in Fig. 2 corresponds to the optimum composition of the suspension for attaining the maximum yield of coating — approximately 10% of the mass

TABLE 1

Sample	Composition of suspension, %		Degassing time, min	Without evacuation		With evacuation	
	$AlO(OH) \cdot nH_2O$	H_2O		Δm_1,* %	Δm_2,** %	Δm_1, %	Δm_2, %
1	10	90	10	–	1.1	20	1.5
2	20	80	30	17	1.5	21	2.2
3	23	77	30	–	1.6	22	2.5
4	25	75	10	19	3.3	23	3.7
5	26	74	10	20	2.6	24	3.0

* Δm_1 — amount of suspension adsorbed on BCS during impregnation.

** Δm_2 — yield of coating on BCS.

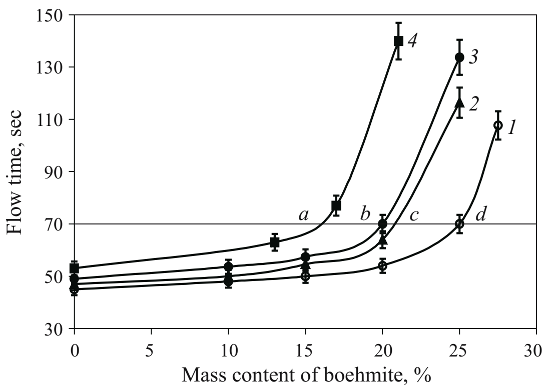

Fig. 2. Flow time of 100 ml suspension through an opening 2 mm in diameter and 2 mm high as a function of the concentration of AlO(OH) in suspensions with dispersion media: *1*) water; *2*) 50% aqueous solution of $Ce(NO_3)_3H_2O$; *3*) aqueous solution of 50% $Ce(NO_3)_3 \cdot 6H_2O$ + 5% $C_{12}H_{22}O_{11}$; *4*) aqueous solution of 50% $Ce(NO_3)_3 \cdot 6H_2O$ + 20% $C_{12}H_{22}O_{11}$.

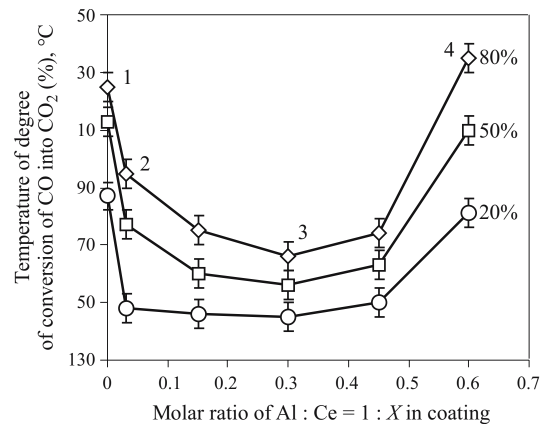

Fig. 3. Effect of the Ce content on the activity of the catalyst of the $Pt - CeO_2 - \gamma\text{-}Al_2O_3$ system on BCS in oxidation of CO by oxygen in a model gas mixture of the composition (volume content, %): 0.3 CO, 0.3 O_2, remainder N_2 at a gas load of 20,000 m^3/h per 1 m^3 of catalyst: *1 – 4*) sample numbers.

of the BCS with a coating. The H_2O : AlO(OH) molar ratio was about 12 : 1 in suspensions 1 – 4 for a flow time of 70 sec (points *a*, *b*, *c*, *d*). These parameters can be used to obtain a uniform layer of suspension on the surface of the BCS and facilitate removal of residues of the suspension from the channels in the block in centrifugation.

The use of a multicomponent suspension with maltose makes it possible to combine the stages of heat treatment of the coating and reduction of the platinum from CPA to the metallic state. The XPA analysis of the coatings after heat treatment at 550°C showed that aluminum oxide is represented by the $\gamma\text{-}Al_2O_3$ phase and cerium oxide is represented by the cubic modification of CeO_2. The specific surface area of the coatings was 150 – 170 m^2/g. Based on a quantitative analysis of the composition of the suspensions and coatings, we found that the Pt : Ce : Al ratio in the suspension and in the coating on BCS coincide.

However, the activity of the block catalyst is the basic criterion of the quality of the catalytic coating. To study this, we created a continuous laboratory unit. Data on the change in the degree of conversion of CO into CO_2 as a function of the Ce : Al molar content in the coating are shown in Fig. 3. The compositions of the suspensions and catalytic coatings obtained on BCS are reported in Table 2. As Fig. 3 shows, the catalyst with a multicomponent coating with a molar ratio of Al : Ce = 1 : 0.3 exhibited the highest activity. The degree of conversion of CO into CO_2 attained the 80% level at 165°C.

The compositions and basic parameters of degassing of aqueous suspensions to increase the yield of coatings on BCS were thus optimized. The effect of the cerium oxide content on the activity of catalysts of the $Pt - CeO_2 - \gamma\text{-}Al_2O_3$ system on BCS in oxidation of CO with oxygen in a gas mixture was established on a continuous laboratory setup. The catalysts exhibited high activity in the 150 – 200°C temperature region.

In our opinion, the results of the study can be used to improve existing suspension methods of fabricating nanostructure materials and coatings on ceramic supports of honeycomb structure made of thermostable ceramic materials, including cordierite. The methodological principles of formation of multicomponent highly porous catalytic coatings from mixed aluminum and cerium oxides containing metallic platinum particles by the suspension method were developed. The use of maltose in multicomponent boehmite suspensions at a molar ratio of (Al + Ce) : $C_{12}H_{22}O_{11}$ = 16 : 1 allows obtaining highly disperse coatings with a mass ratio of $Al_2O_3 : CeO_2$ = 1 : 1 in one stage of application and heat treatment, and their properties cause the high activity of the block catalysts in treatment of gases.

TABLE 2

Sample	Molar ratio in suspension			$Al_2O_3 : CeO_2$ mass ratio in coating	Yield of coating on BCS, wt.%	Specific surface area of coating, m^2/g
	Al : Ce	Pt : $C_{12}H_{22}O_{11}$	Al + Ce : $C_{12}H_{22}O_{11}$			
1	Without CeO_2	1 : 4	–	Without CeO_2	5 – 6	254
2	1 : 0.03	1 : 4	–	1 : 0.1	7 – 8	240 – 260
3	1 : 0.30	1 : 4	16 : 1	1 : 1	7 – 8	140 – 170
4	1 : 0.60	1 : 4	8 : 1	1 : 2	7 – 8	100 – 110

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